

Network topology approach to new allotropes of the group 14 elements

Lars Öhrström^{*,1} and Michael O’Keeffe^{II}

^I Dept. of Chemical and Biological Engineering, Physical Chemistry, Chalmers University of Technology, 412 96 Göteborg, Sweden,

^{II} Michael O’Keeffe, Dept. of Chemistry & Biochemistry, Arizona State University, Tempe, 85287, USA
and Graduate School of EEWS(WCU), KAIST, 373-1, Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea

Received March 9, 2013; accepted May 24, 2013

Published online: July 8, 2013

Allotrope / Group 14 / Topology / 3D-network

Abstract. The network topology approach has been a major driving force in the search for new metal-organic frameworks and coordination networks. In this work we demonstrate how this method not only generated the recently described “T12” allotrope of the group 14 elements, identical to the **cdp** topology found in the structure of CdP₂, but also a number of other candidate structures for polymorphs of these network-forming elements. Data on such network structures have been compiled since the 1950’s and is readily accessible through several internet based systems. The usefulness of topology for the classification of these allotropes is emphasised.

1. From metal-organic frameworks to the pure elements

It is obvious that not all chemical compounds are created equal; some are clearly more equal than others. We are especially intrigued it appears, by new forms of the group 14 elements. This is partly due to the technological importance of these materials, for example the promising applications of graphene and the use of silicon and germanium in semiconductors. But it is also due to a fascination with finding new forms of an element known to man since ancient times.

Recently a new tetragonal allotrope of the group 14 elements, the T12 phase, was reported. This allotrope was proposed based on elaborate computational methods, accounting for some experimental results in synthesized metastable phases [1]. It occurred to us that purely geometrical considerations of possible network topologies, as pioneered by Wells [2–3] and extended by O’Keeffe and Hyde [4] and later by O’Keeffe and Delgado-Friedrichs [5], could be of use in searching for such polymorphs.

For Metal-Organic Frameworks, Coordination Networks and related areas of crystal engineering this method has been immensely successful in several respects. It has been used to reduce seemingly complicated structures in

molecular magnetism and hydrogen bonded self-assembly to graspable entities significantly enhancing the understanding of the structure [6–9], to clarify the intermolecular forces acting within a crystal in hydrogen bonded systems [10], to identify non-obvious relationships between different MOFs [11], and to act as blueprints for the synthesis of new materials [12–13].

Finally, and more pointedly for the subject of this communication, is that the topology approach significantly narrows down possible structures of a new material, given that the starting materials contain the appropriate parts for secondary building units (SBUs) of a distinct topology. For compound classes where single crystals of good quality can routinely be obtained this may not be of great importance, but it has been used to great advantage to obtain atomic resolution structures from powder diffraction data for covalent organic frameworks [14]. Another field where it is conspicuously difficult to obtain good crystals is, of course, the everlasting search for new allotropes of the pure elements, frequently obtained under nonstandard conditions.

2. Network analysis of the Si T12 allotrope

Indeed, it was a five minutes procedure, using the program Systre [15], to identify the Si T12 allotrope with the network topology known as **cdp**, found in the structure of CdP₂ and described in detail by O’Keeffe and Hyde in 1996 [4]. (In this work nets are identified by the bold three-letter symbols used in the Reticular Chemistry Structure Resource, RCSR [16–17].)

From a chemical point of view it should be noted that CdP₂ has 48 valence electrons per unit cell, *i.e.* 4 per atom just like Si, and that the structure has (only) 5-, 6-, and 7-rings. The 5- and 7-rings occur in equal numbers so the average ring size is 6 – just like the diamond Si structure (the **dia** net).

More importantly, the three different bonds of the **cdp** topology can be made equal. This means that the bond energy penalty on the total thermodynamic stability of this phase due to the impossibility to achieve optimal geome-

* Correspondence author (e-mail: ohrstrom@chalmers.se)

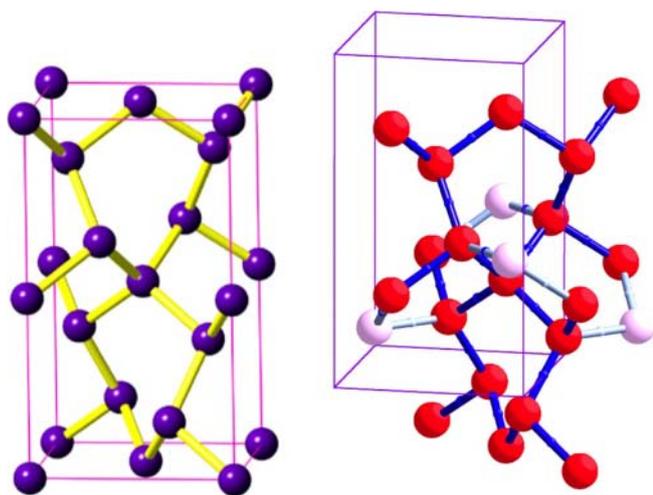


Fig. 1. The Si T12 phase (left, Reprinted with permission from Zhao, Z.; Tian, F.; Dong, X.; Li, Q.; Wang, Q.; Wang, H.; Zhong, X.; Xu, B.; Yu, D.; He, J.; Wang, H.-T.; Ma, Y.; Tian, Y. *J. Am. Chem. Soc.* **2012**, *134*, 12362. © (2012) the American Chemical Society) and the ideal **cdp** net from the RCSR database. The network structure has been emphasized in the latter, showing both the six- and five-membered rings (but not the seven-membered rings). The pink atoms and light blue bonds in the **cdp** net do not appear in the picture of the Si T12 structure.

try will be low and only depend on the deviations from ideal tetrahedral bond angles. These differ from the ideal tetrahedron as the minimum angles are 101.9° and maximum angles 123.6° , with an average of 109.2° , but these deviances typically affect the overall bond enthalpy only to a small degree.

3. The general case of group 14 allotropes

3.1 Research tools for network analysis

The structures of the most common allotropes based on 3D-networks of the group 14 elements, such as diamond, are based on tetrahedral coordination, typically sp^3 - sp^3 bonds. By coincidence so are the ubiquitous zeolite structures and much effort has been devoted to collecting and classifying real and hypothetical zeolite networks [18–19]. Extensive collections exist such as the zeolite database [20], and four coordinated nets can be searched also in the Reticular Chemistry Structural Resource (RCSR) database [16–17], and in the EPINET project that is more mathematically oriented [21–22]. In certain cases, *vide infra*, three-coordination may also be considered, and the two latter databases contain parameters for nets of coordination numbers up to twelve.

The RCSR database is also included in the Systre program [15] but the most versatile program for analysing network topologies and related properties of materials with known structures (unit cell, space group and coordinates) is TOPOS [23, 24], also incorporating the RCSR database supplemented with an even larger collection of network topologies found in real compounds.

Numerous guides and tutorials are available in monograph form [3, 4, 25, 26], book chapters [27, 28], and in the chemical Refs. [5, 17, 29–32].

3.2 Theoretical background

The nets for hypothetical group 14 element structures will most likely be those of n -coordinated sphere packings. That is, the nets have embeddings (space group) in which the n shortest distances between vertices (atom positions) are equal and correspond to edges of the nets.

One might further suppose that candidate structures have angles close to the tetrahedral angle. This excludes structures with 3- or 4-rings, although we note that a 4-ring structure was very recently reported for germanium [33].

All uninodal (with only one type of vertex) 4-coordinated structures of the type sought (sphere packings without 3-rings and 4-rings) were enumerated some years ago by O’Keeffe and Brese [34]. These authors identified 24 such structures that were still 4-coordinated sphere packings in their minimum density embedding. One overlooked structure (RCSR symbol **mmt**) was subsequently found by Treacy [35]. All 25 are identified in the RCSR.

Independent work by Werner Fischer and associates has identified all uninodal sphere packings other than those with monoclinic symmetry [36, 37]. 805 of these are to be found in the RCSR which also provides references.

Not all of the 25 nets mentioned above are suitable as low-energy elemental structures, however. For example, the structure with symbol **cds** has an embedding as a sphere packing, but in its minimum density configuration each vertex has six equidistant neighbours.

3.3 Possible allotropes based on topology considerations

The subset of these nets in which non-bonded distances are greater than 1.4 times the bond length is readily found from the RCSR. This is, for carbon, substantially shorter than two times the van der Waals radius, but still a suitable cut-off value. In diamond itself, the shortest non-bonded distance is 1.63 times the C–C bond length, or 2.52 Å.

Excluding structures with square coordination such as **nbo**, eleven of these are presented in Table 1. These seem to us the most probable topologies for allotropes of the group 14 elements forming three-dimensional networks. We also include a few binodal nets in this table.

Writing NaGaSn_5 as a Zintl compound $\text{Na}^+(\text{Ga}^-\text{Sn}_5)$ one can see that the part in parentheses as four valence electrons per atom, thus corresponding to the group 14 elements. The corresponding **unj** net was in fact identified as a possible low energy carbon structure by Pickard and Needs [38].

Other proposed 4-coordinated carbon structures in the RCSR include two four-nodal (vertex 4-transitive) structures **cbn**, (M-carbon) [39] and **cnw**, (carbon –W) [40]. Note that to enumerate all possibilities up to vertex 4-transitive seems conceivable, but that the number is likely to be of the order of 10^5 – 10^6 [5].

The RCSR also contains 51 3-coordinated sphere packings. The 36 of those without 3- and/or 4-rings are candidates for sp^2 carbons. One, **pbz** (“polybenzene”), is the lowest energy hypothetical carbon (significantly lower in energy than C_{60}) [41]. Another net, **srs**, considered as a

Table 1. The most probable topologies for allotropes of the group 14 elements based on the deviation of the bond angles from the ideal tetrahedral angle ($\Delta\alpha$), shortest non-bonding interaction (C...C) and network density. Data from the ideal 3D nets in the RCSR database [16, 17]. Examples of occurrence in allotropes or simple compounds are also given. All data scaled with, and compared to, the diamond structure.

Net	$\Delta\alpha$ (°C)	C...C (Å)	Dens.	Example
dia	0.00	2.52	0.65	diamond
lon	0.00	2.52	0.65	lonsdaleite
cfc ¹	0.00	2.52	0.65	carbon 4C
gsi	11.5	2.18	0.74	γ -Si
cdp ¹	14.1	2.39	0.63	Si T12
unj	15.4	2.43	0.60	NaGaSn ₅ ⁵
uni	15.7	2.25	0.68	
unb	15.9	2.25	0.68	
neb	18.9	2.23	0.73	
crb ³	19.5	2.18	0.62	
pcb ⁴	19.5	2.18	0.51	carbon C8
sie ²	19.5	2.18	0.64	Si-8
qtz	22.33	2.18	0.75	quartz
les	22.34	2.35	0.69	
und	26.26	2.22	0.68	
unc	26.3	2.22	0.68	

1: Binodal, 2: Binodal, contains 4-rings, 3: Zeolite type BCT, 4: Zeolite type ACO, 5: GaSn₅ net.

possible carbon allotrope by these authors is ubiquitous in chemistry, but generally unknown to mathematicians and physicists [42].

Another structure proposed, C8, is also binodal [43, 44], whereas the “topological stacking” method of different carbon fragments recently proposed, yielded four-nodal nets as potential allotropes [45]. We note that such four nodal nets are rare when combining high symmetry building blocks, and even in molecular chemistry, where deliberate symmetry breaking molecules or even two or more different building blocks are used, they are seldom found [46].

In principle, rough estimates of the thermodynamic stability of these structures is available by the use of the standard intramolecular potentials used in molecular mechanics calculations. Thus the bond stretching, bending and torsion potentials are well-known and even van der Waals interactions can be included. Alternatively these structures can be used as convenient starting points for more elaborate calculations.

A further possibility should also be mentioned, networks may interpenetrate forming two or more interwoven but non-connected nets in the structure, a common feature for coordination networks [47–49].

4. Conclusions

In conclusion we want to point out the wealth of geometrical information available for all kinds of network compounds be they elemental, binary, zeolites or coordination

networks. These can be used as blueprints for new synthetic endeavours or as starting point for structure elucidation of existing phases.

Last but not least we want to mention the classification and communication advantages of network topologies. This is an unambiguous way to classify and communicate data for new and old phases of the group 14 elements and makes comparisons between them easier. The approach has been used extensively in crystal engineering and proved to be very successful [27].

Moreover, recent provisional IUPAC recommendations strongly suggest the use of topology descriptors and names in the field of coordination networks and metal-organic frameworks [50], and we feel these would be equally advantageous for reporting and discussing allotropes of the group 14 elements.

Acknowledgement. LÖ is grateful for support from the Swedish Research Council. MOK is supported by the World Class University program (R-31-2008-000-10055-0) and by the U.S. National Science Foundation DMR 1104798.

References

- [1] Z. Zhao, F. Tian, X. Dong, Q. Li, Q. Wang, H. Wang, X. Zhong, B. Xu, D. Yu, J. He, H.-T. Wang, Y. Ma, Y. Tian, Tetragonal Allotrope of Group 14 Elements, *J. Am. Chem. Soc.* **2012**, *134*, 12362–12365.
- [2] A. F. Wells, The geometrical basis of crystal chemistry. I, *Acta Cryst.* **1954**, *7*, 535–544.
- [3] A. F. Wells, *Wiley Monographs in Crystallography Series: Three-Dimensional Nets and Polyhedra.*, John Wiley and Sons, New York, N. Y., **1977**.
- [4] M. O’Keeffe, B. G. Hyde, *Crystal Structures I: Patterns and Symmetry*, Mineral Soc. Am., Washington, **1996**.
- [5] O. Delgado-Friedrichs, M. D. Foster, M. O’Keeffe, D. M. Proserpio, M. M. J. Treacy, O. M. Yaghi, What do we know about three-periodic nets?, *J. Solid State Chem.* **2005**, *178*, 2533–2554.
- [6] Q. Y. Zhu, A. M. Arif, L. Öhrström, J. S. Miller, Syntheses, structure, and magnetic properties of extended structured Cr(II) pentacyanopropenide compounds, *J. Mol. Struct.* **2008**, *890*, 41–47.
- [7] A. F. Wells, The geometrical basis of crystal chemistry. Part 3, *Acta Cryst.* **1954**, *7*, 842–848.
- [8] C.-J. Wallentin, E. Orentas, M. T. Johnson, E. Butkus, O. Wendt, L. Öhrström, K. Wärnmark, Network analysis of bicyclo[3.3.1]nonanes: the diol, the dione and the acetal, *CrystEngComm* **2009**, *11*, 1837–1841.
- [9] F. Luo, Y. X. Che, J. M. Zheng, Highly Rare Ferromagnetic Interaction with the Cu(tetrahedron)-Cu(square)-Cu(tetrahedron) Mode Observed in A 2-Fold Interpenetrating Moganite Net, *Cryst. Growth Des.* **2009**, *9*, 2047–2049.
- [10] M. A. M. Abu-Youssef, V. Langer, L. Öhrström, A unique example of a high symmetry three- and four-connected hydrogen bonded 3D-network, *Chem. Comm.* **2006**, 1082–1084.
- [11] K. Davies, S. A. Bourne, L. Öhrström, C. L. Oliver, Anionic zinc-trimesic acid MOFs with unusual topologies: Reversible hydration studies, *Dalton Trans.* **2010**, *39*, 2869–2874.
- [12] A. C. Sudik, A. P. Cote, O. M. Yaghi, Metal-organic frameworks based on trigonal prismatic building blocks and the new “acs” topology, *Inorg. Chem.* **2005**, *44*, 2998–3000.
- [13] Y. B. Zhang, W. X. Zhang, F. Y. Feng, J. P. Zhang, X. M. Chen, A Highly Connected Porous Coordination Polymer with Unusual Channel Structure and Sorption Properties, *Angew. Chem. Int. Ed.* **2009**, *48*, 5287–5290.
- [14] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Cote, R. E. Taylor, M. O’Keeffe, O. M. Yaghi, Designed synthesis of 3D covalent organic frameworks, *Science* **2007**, *316*, 268–272.

- [15] O. Delgado Friedrichs, Systre 1.1.4beta, <http://gavrog.sourceforge.net/>, accessed 5th March 2013. O. Delgado Friedrichs, M. O'Keeffe, *Acta Crystallogr.* **2003**, A60, 351–360.
- [16] M. O'Keeffe, O. M. Yaghi, S. Ramsden, Reticular Chemistry Structure Resource, Australian National University Supercomputer Facility, <http://rcsr.anu.edu.au/>, accessed 5th March 2013.
- [17] M. O'Keeffe, M. A. Peskov, S. Ramsden, O. M. Yaghi, The Reticular Chemistry Structure Resource (RCSR) Database of, and Symbols for, CrystalNets, *Acc. Chem. Res.* **2008**, 41, 1782–1789.
- [18] J. V. Smith, Topochemistry of Zeolites and Related Materials. 1. Topology and Geometry, *Chemical Reviews* **1988**, 88, 149–182.
- [19] M. A. Zwiijnenburg, S. T. Bromley, M. D. Foster, R. G. Bell, O. Delgado-Friedrichs, J. C. Jansen, T. Maschmeyer, Toward understanding the thermodynamic viability of zeolites and related frameworks through a simple topological model, *Chem. Mater.* **2004**, 16, 3809–3820.
- [20] The Structure Commission of the International Zeolite Association (IZA-SC), <http://www.iza-structure.org/> accessed 5th March 2013.
- [21] S. J. Ramsden, V. Robins, S. Hungerford, S. T. Hyde., epinet.anu.edu.au, accessed 5th March 2013. S. J. Ramsden, V. Robins and S. T. Hyde, *Acta Crystallogr.* **2009**, A65, 81–108.
- [22] S. Hyde, O. D. Friedrichs, S. J. Ramsden, V. Robins, Towards enumeration of crystalline frameworks: the 2D hyperbolic approach, *Solid State Sciences* **2006**, 8, 740–752.
- [23] V. A. Blatov, Nanocluster analysis of intermetallic structures with the program package TOPOS, *Struct. Chem.* **2012**, 23, 955–963.
- [24] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, TOPOS 4.0, Ac.Pavlov St. 1, 443011 Samara, Russia <http://www.topos.samsu.ru/>, accessed 15th May 2013.
- [25] S. R. Batten, D. R. Turner, M. S. Neville, *Coordination Polymers: Design, Analysis and Application*, RSC, Cambridge, **2009**.
- [26] L. Öhrström, K. Larsson, *Molecule-Based Materials The Structural Network Approach*, Elsevier, Amsterdam, **2005**.
- [27] L. Öhrström, in *Encyclopedia of supramolecular chemistry, Vol. 8. Supramolecular materials chemistry* (Ed.: L. Barbour), Wiley Chichester, UK, **2012**.
- [28] V. A. Blatov, D. M. Proserpio, in *In Modern Methods of Crystal Structure Prediction* (Ed.: A. R. Oganov), Wiley-VCH, Weinheim, **2011**.
- [29] O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, Taxonomy of periodic nets and the design of materials, *Phys. Chem. Chem. Phys.* **2007**, 9, 1035–1043.
- [30] M. O'Keeffe, M. Eddaoudi, H. L. Li, T. Reineke, O. M. Yaghi, Frameworks for extended solids: Geometrical design principles, *J. Solid State Chem.* **2000**, 152, 3–20.
- [31] M. O'Keeffe, O. M. Yaghi, Reticular chemistry – Present and future prospects – Introduction, *J. Solid State Chem.* **2005**, 178, V–VI.
- [32] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, *Nature*, **2003**, 423, 705–714.
- [33] D. Selli, I. A. Baburin, R. Martonak, S. Leoni, Novel metastable metallic and semiconducting germaniums, *Scientific Reports* **2013**, 3, 1466.
- [34] M. O'Keeffe, N. E. Brese, Uninodal 4-connected 3D nets – Nets without 3-rings or 4-rings, *Acta Cryst. A* **1992**, 48, 663–669.
- [35] M. M. J. Treacy, K. H. Randall, S. Rao, J. A. Perry, D. J. Chadi, Enumeration of periodic tetrahedral frameworks, *Z. Kristallogr.* **1997**, 212, 768–791.
- [36] W. Fischer, Tetragonal sphere packings: minimal densities and subunits, *Acta Cryst. A* **2005**, 61, 435–444.
- [37] H. Sowa, Orthorhombic sphere packings. IV. Trivariant lattice complexes of space groups without mirror planes belonging to crystal class mmm, *Acta Cryst. A* **2012**, 68, 763–777.
- [38] C. J. Pickard, R. J. Needs, Hypothetical low-energy chiral framework structure of group 14 elements, *Phys. Rev. B* **2010**, 81.
- [39] Q. Li, Y. M. Ma, A. R. Oganov, H. B. Wang, H. Wang, Y. Xu, T. Cui, H. K. Mao, G. T. Zou, Superhard Monoclinic Polymorph of Carbon, *Phys. Rev. Lett.* **2009**, 102.
- [40] J. T. Wang, C. F. Chen, Y. Kawazoe, Low-Temperature Phase Transformation from Graphite to sp(3) Orthorhombic Carbon, *Phys. Rev. Lett.* **2011**, 106, 075501.
- [41] M. O'Keeffe, G. B. Adams, O. F. Sankey, Predicted new low-energy forms of carbon, *Phys. Rev. Lett.* **1992**, 68, 2325–2328.
- [42] S. T. Hyde, M. O'Keeffe, D. M. Proserpio, A Short History of an Elusive Yet Ubiquitous Structure in Chemistry, Materials, and Mathematics, *Angew. Chem. Int. Ed. Eng.* **2008**, 47, 7996–8000.
- [43] J. H. Zhai, D. L. Yu, K. Luo, Q. Q. Wang, Z. S. Zhao, J. L. He, Y. J. Tian, Metastable C-centered orthorhombic Si-8 and Ge-8, *J. Phys. Cond. Mat.* **2012**, 24.
- [44] Z. S. Zhao, B. Xu, X. F. Zhou, L. M. Wang, B. Wen, J. L. He, Z. Y. Liu, H. T. Wang, Y. J. Tian, Novel Superhard Carbon: C-Centered Orthorhombic C-8, *Phys. Rev. Lett.* **2011**, 107.
- [45] H. Y. Niu, X. Q. Chen, S. B. Wang, D. Z. Li, W. D. L. Mao, Y. Y. Li, Families of Superhard Crystalline Carbon Allotropes Constructed via Cold Compression of Graphite and Nanotubes, *Phys. Rev. Lett.* **2012**, 108, 135501.
- [46] N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, Reticular Chemistry: Occurrence and Taxonomy of Nets and Grammar for the Design of Frameworks. *J. Am. Chem. Soc.* **2005**, 38, 176–182.
- [47] S. R. Batten, Topology of Interpenetration, *CrystEngComm* **2001**, 3, 67.
- [48] V. A. Blatov, L. Carlucci, G. Giani, D. M. Proserpio, Interpenetrating metal-organic and inorganic 3D network: a computer-aided systematic investigation. Part I. Analysis of the Cambridge structural Database, *Cryst Eng Comm* **2004**, 6, 377–395.
- [49] I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, Interpenetrating metal-organic and inorganic 3D networks: a computer-aided systematic investigation. Part II. Analysis of the Inorganic Crystal Structure Database (ICSD), *J. Solid State Chem.* **2005**, 178, 2452–2474.
- [50] S. R. Batten, N. R. Champness, X. M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh, J. Reedijk, Terminology of Metal-Organic Frameworks and Coordination Polymers (IUPAC provisional recommendations 2013) *Pure and Appl. Chem.* **2013**, in press.